

THE ANALYST.

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SUMMER EXCURSION.

The arrangement of last year, that the Society should make London the starting point of their summer excursion, having proved so successful, it was decided to adopt a similar course this time. Dr. Ashby had some time since expressed himself desirous of entertaining the Society during a portion of the day, and in order to enable the party to avail themselves of his kind invitation, it was determined that the excursion should again take the form of a river trip—starting above Reading, exploring the upper reaches of the Thames, and returning to Dr. Ashby's house at Reading. The party (numbering some 30 members and friends, and including a fair proportion of ladies), met at Paddington and travelled to Goring, where a steam-launch was waiting to convey them to Wallingford. Arriving here, they sat down to an excellent luncheon at the Lamb Hotel, followed by some humorous speeches from the President, Mr. Allen and Mr. Cassal. The launch was again boarded and the party steamed down to Reading, where carriages were in readiness to convey them to Dr. Ashby's residence. An out-door entertainment in the form of a garden party was provided; several hours were agreeably spent in perambulating Dr. Ashby's charming and picturesque grounds, and in enjoying the refreshments so liberally provided. A vote of thanks to Dr. and Mrs. Ashby for their kindness was proposed and carried with acclamation, after which the party were conveyed to Reading station, whence they took train for Paddington, arriving there about 11 o'clock. The weather was all that could be desired, and a thoroughly enjoyable day was spent. Several photographs of the party were taken by Messrs. Chattaway and Stansell.

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS.

A Special Meeting of the Society was held on Thursday, 30th June, at the rooms of the Society of Arts, John Street, Adelphi, the President (Mr. Otto Hehner) in the chair.

The following gentlemen were proposed as Members:—Messrs. Gustave Antonio Abrines, F.C.S., E. J. Bevan, and John Bate Nickolls.

Dr. A. P. Aitken, 8, Clyde Street, Edinburgh, and Mr. Frederick William Tompson, F.C.S., Stapenhill Road, Burton-on-Trent, were duly elected Members of the Society.

Mr. J. Williams, Government Laboratory, Georgetown, Demerara, British Guiana, was duly elected an Associate.

Mr. Allen temporarily took the chair whilst the President read a paper "On the Estimation of Olein," which was followed by a discussion.

The President having resumed the chair, Mr. A. H. Allen read a paper entitled "Experiments on the Alkaloid of Tea," and, after the paper had been discussed, Dr. Teed read the following paper:—

THE DETECTION AND ESTIMATION OF MINUTE QUANTITIES OF LEAD IN THE PRESENCE OF COPPER AND IRON.

By FRANK L. TEED, D.Sc.

I propose first to refer to the detection of lead in sulphuric acid. The usual method is by dilution with water, but I found, some years ago, that by adding hydrochloric acid to the sulphuric acid, and keeping it cold, a much smaller quantity of lead could be detected than by adding water, or even by adding water and subsequently an equal volume of absolute alcohol. The lead is precipitated as chloride as a peculiar pearly opalescence. I patented this process for the purpose of removing lead from sulphuric acid, which it does perfectly, but sulphuric acid manufacturers assure me that there is no commercial value in any process that would effect such a result. Although leaving something to be desired as a patent, the process is still of use as a test on account of its delicacy. It can be applied to the detection of minute quantities of lead in organic substances. Take, for instance, a substance which is generally, I may say invariably, contaminated with lead—tartaric acid. The lead is a little difficult of detection by the ordinary process, because sulphide of lead, as we know, is more or less soluble in tartaric acid. If the tartaric acid is ignited, a large proportion of the lead is, of course, lost, but some is left, and there is sufficient in the small quantity of ash, if digested with pure sulphuric acid, to show the characteristic reaction on the subsequent addition of hydrochloric acid. While on the use of hydrochloric acid as a test for lead in sulphuric acid, I may mention that nitric acid is also a test for lead in sulphuric acid; but it is not nearly so delicate as hydrochloric acid. If to a sample of commercial sulphuric acid which is very rich (*i.e.*, very impure) in lead, nitric acid is added, the lead mainly settles out, but still, after treatment with nitric acid, lead can be detected by the addition of hydrochloric acid. Hydrochloric acid gas is insoluble in sulphuric acid, and if passed through strong sulphuric acid which is highly contaminated with lead, for an hour or more, nothing whatever happens, but if to that acid in a test tube a single drop of the solution of hydrochloric acid, or a crystal of common salt is added, the characteristic precipitate at once appears.

The main object of my paper was to draw attention to the difficulty of detecting and estimating minute quantities of lead in presence of copper and iron. There are certain temperance drinks, such as lemonade and soda water, which, in the process of manufacture, are liable to contain at least these three metallic impurities.

In the case of lemonade, the lead occurs partly in the tartaric acid used, and partly comes from the use, perhaps one ought to say abuse, of lead pipes for transferring the charged solutions; and the copper comes from the copper cylinders (although tin-lined) in which the drink is charged with carbonic acid. Hence the difficulty arises of detecting a highly poisonous metal like lead, in the presence of a mildly poisonous metal like copper, and a non-poisonous metal like iron. The most delicate reaction for both lead and copper is, I believe, the precipitation as sulphides, either by sulphuretted hydrogen or ammonium sulphide. The amounts present can, of course, be estimated colorimetrically by comparison with known quantities. I find the sulphide reaction far more delicate in the case of copper than the ferro-cyanide reaction. I do not think the hundredth of a grain of copper in a gallon of liquid could be detected by means of the ferro-cyanide reaction without concentration, but ammonium sulphide would easily detect it. The objection to this reagent is that it does not distinguish between lead and copper. To effect this distinction I simply make use of the well-known fact that sulphide of copper is soluble in cyanide of potassium, whereas sulphide of lead is not. To perform a determination:—Place a measured quantity of lemonade, or other liquid, in a cylinder or white basin. Add a few c.c. of ammonia and a little cyanide of potassium, then add a minute quantity of ammonium sulphide. Down comes the lead, but not the copper. Then imitate the colour by known quantities of lead precipitated under similar conditions. Iron does not at all interfere with the test. If an iron salt is added to lemonade, for instance, and made alkaline with ammonia, the iron is kept in solution by the tartaric acid, and on addition of cyanide of potassium is converted into a ferro or ferri-cyanide, not precipitable by ammonium sulphide. In the case of liquids not containing tartaric acid, it is easy enough to add a little in the event of iron being present.

DISCUSSION.

Mr. Bertram Blount said that with reference to the general question of testing for lead in small quantities, that there was one test, the merits of which Mr. Allen and Mr. Harvey had done much to make known. He referred to the chromate test, which he constantly used for all purposes; it was not only exceedingly delicate if properly carried out, but also extremely characteristic.

Mr. Sidney Harvey said that in water containing a fiftieth part of a grain of lead per gallon, the metal could be precipitated by bichromate of potash. If allowed to stand for 12 hours the water could be poured off to the last drop, and the chromate of lead could then be advantageously stirred up with a little distilled water and turned into a smaller vessel, say a half-inch test tube, when a precipitate visible both by colour and amount would quickly settle.

Mr. E. Russell Budden said he had found that when the chromate test was used in the presence of organic matter, a reduction always took place. For instance, in a case of testing for lead in lemonade, if one used the chromate test with the original liquid, and allowed it to stand for a time, in a great many cases, presumably from the fact of

tartaric acid or other reducing agents being present, a green chromium salt was produced, and the chromate precipitate was practically unobservable. He did not know whether any of the members had observed the same thing, but it had been an insuperable difficulty with him in applying the test in presence of organic matter. Whilst speaking of the chromate test, he would mention that he had adopted the method of observing it under different conditions of light to those usually recommended. He believed the usual method was to place the water in a cylinder or vessel of some kind to allow of settlement and decantation. He had found that if the test were observed in an ordinary light, very frequently a *minute* trace of lead escaped observation; but if the light were shed in such a way that an oblique beam fell through the liquid, all other light being excluded, a characteristic opalescence could be detected. He used a square box sufficiently large to contain a good sized flask, and so constructed that the light came only through an aperture in the upper part. By adopting this method, he was able to detect exceedingly minute quantities of lead in waters, quantities which, without these precautions, the method utterly failed to give any indication of. He had been worrying over this matter for a very long time, and had tried the experiment in presence of copper and other metals. In addition to the two or three metals mentioned by Dr. Teed, tin was occasionally present in artificial mineral waters; and he had also found traces of antimony. He believed the President could bear him out so far as the tin was concerned.

Dr. Teed, in reply, said that he was obliged, in testing lemonades, to abandon the chromate test for reasons similar to those mentioned by Mr. Budden. He would like to know whether Mr. Blount or any other member had personal experience with the chromate test in presence of tartaric acid or other organic matters, such as occurred in commercial lemonades. With regard to the presence of tin and antimony, they would not interfere with the test for lead, it being performed in an alkaline solution with ammonium sulphide as the precipitant.

Dr. Sykes read a paper "On a deposit found in Fermenting Vats," after which Mr. Richmond read the following paper:—

LEFFMANN AND BEAM'S METHOD OF FAT ESTIMATION IN MILK.

PART I.

By H. DROOP RICHMOND.

LEFFMANN and Beam (*THE ANALYST*, xvii., 83) have recently described a method, a modification of the Babcock centrifugal method, for fat estimation in milk.

Hehner (*THE ANALYST* xvii., 102) reports favourably on it; he presumes that the layer measured is not pure butter fat, but is a mixture of fat and fusel oil.

In the discussion on Hehner's paper, Allen was of opinion that in order to get accurate results the temperature should be taken into account; I pointed out that the factor used by Leffman and Beam (0.86) was probably obtained by dividing 0.89, the density of butter fat at 50° or 60°, by 1.032, the average density of milk.

I have lately, by the kindness of the President in lending me his machine, had the opportunity of investigating this method. I must withdraw my former opinion mentioned above, as I find that the temperature of the fat is about 25° to 30° when measured, and therefore, if pure butter fat, the density would be about 0.92, instead of 0.89; this is evidence that the layer measured is not pure butter fat.

My experiments may be divided into three series:—

- I. With bottles received from Messrs. Leffmann and Beam, graduated in 100 parts, and using ordinary fusel oil.
- II. With bottles made by Messrs. Müller and Co., 148, High Holborn, graduated so that 86 divisions = 1.475 c.c., and using ordinary fusel oil.
- III. With bottles as in II., and using pure amyl alcohol from Hopkin and Williams, 16, Cross Street, Hatton Garden.

They were compared with fat estimated by the Adams (A), Wanklyn (W), Schmidt (S), and Carter-Bell (C-B) processes, and, in the case of creams, the fat calculated by Vieth's table (V) (*THE ANALYST*, ix., 64).

Creams were analysed by measuring 10 c.c. in a 10 c.c. specific gravity bottle, diluting it to 50 c.c., and taking 15 c.c. of this mixture; the results were calculated by the following table:—

Reading.	Percentage of cream.	Reading.	Percentage of cream.
40	18.4	70	34.8
45	21.1	75	37.6
50	23.8	80	40.4
55	26.5	85	43.2
60	29.3	90	46.0
65	32.0	95	48.8

The results obtained were:—

Series I.

		Fat.		
No.		Gravimetric.	L and B.	Error.
1.	...	3.22	3.27	+ .05
2.	...	3.36	3.53	+ .17
3.	...	3.52	3.61	+ .09
4.	...	3.58	3.53	— .05
5.	...	3.76	3.91	+ .15
6.	...	3.36	3.44	+ .08
7.	...	2.70	2.9	+ .20
8.	...	3.68	3.83	+ .15
9.	...	3.96	3.91	— .05
10.	...	.24	.28	+ .04
11.	...	.22	.21	— .01
12.	...	.22	.21	— .01
13.	...	.36	.4	+ .04
14.	...	11.4	11.5	+ .1
15.	...	57.6 V	57.0	— .6
16.	...	26.1 V	26.2	+ .1
17.	...	20.9	{ 20.8	— .1
			{ 21.3	+ .4

All gravimetric determinations, unless otherwise stated, were obtained by the Adams method.

The results in Series I. are good; there is a tendency, on the whole, to obtain slightly higher figures by the centrifugal method. Unfortunately, the bottles used in this series were broken, and I have no means of testing the graduations.

Besides these, I have tested numerous milks and compared them with the calculated results; in no case did the error exceed 0.2 per cent.

Series II.

No.	Fat.			Error.
	Gravimetric.	L and B.	L and B corrected.	
18. ...	2.42	2.65	2.49	+ .07
19. ...	22.0	23.2	21.8	— .2
20. ...	29.4 V	31.7	29.8	+ .4
21. ...	23.8	24.3	22.9	— .1
22. ...	.24	.35	.33	+ .09
23. ...	1.48	1.65	1.55	+ .07
24. ...	2.18	2.4	2.25	+ .07
25. ...	3.98	4.1	3.85	— .15
26. ...	5.04	5.45	5.12	+ .08
27. ...	7.85	8.2	7.70	— .15
28. ...	11.80	{ 13.05 (10 c.c. milk) 12.9 (5 c.c. milk)	12.2	+ .4
29. ...	22.9 V		12.1	+ .3
		25.4	23.9	+ 1.0

The results in this case were too high by the centrifugal method, and were corrected by dividing by 1.065, which gave a satisfactory agreement.

A probable reason for this difference will be given later on.

Series III.

Experiments were first made varying the quantity of the fusel mixture.

A cream was taken, which gave by the Schmidt method 21.4 per cent., and by the Adams 21.4 per cent; average, 21.4 per cent.

			Divisions.	Fat by table.
30. ...	1 c.c. fusel mixture		41.5	
31. ...	3 c.c. " "		45.5	21.2
32. ...	5 c.c.		47.0	

35.0 of a dark liquid.

This 35 divisions was proved to consist essentially of fusel oil, and to equal 0.6 c.c. fusel oil, containing, however, a proportion of acid.

Subtracting, then, this quantity from the quantity added in the 5 c.c., we have in solution :—

in 30	...	...	0.5 c.c. in fusel oil.
" 31	...	...	1.5 c.c. " "
" 32	...	...	1.9 c.c. " "

As the cream contained 21·4 per cent. fat, and the 10 c.c. weighed 1·010 grams, the fat should occupy 40·0 divisions, giving an excess of :—

			Found.	Calculated.
in 30	...	...	1·5 divisions	1·8
„ 31	...	...	5·5 „	5·4
„ 32	...	...	7·0 „	6·8

These are almost in proportion to the quantity of fusel oil, as shown by the figures calculated from the mean ratio.

Another cream, containing 24·0 per cent. fat, gave figures as follows :—

33	...	1 c.c. fusel mixture	47·0 divisions.
34	...	3 c.c. „ „	51·0 „

The fat should occupy 45·0 divisions, showing an excess of :—

				Found.	Calculated.
In 33	...	...	...	2·0	2·0
„ 34	...	...	...	6·0	6·1

The excess is in the same ratio.

When a substance is dissolved in a mixture of two immiscible solvents, it dissolves in each of them if the solutions are not saturated in the ratio of the maximum solubility of each, provided that combination does not take place.

To test this statement 10 c.c. of a solution of mercury chloride were taken and shaken with 15·1 c.c. of ether; after correcting for change of volume, it was found that 10 c.c. of ether contained 0·318 gram, and 10 c.c. of water 0·080 grams, or a ratio of 3·97 to 1·0.

The maximum solubilities are in water 7·4 grams. per 100 c.c., and in ether 30 grams. per 100 c.c., or a ratio of 4·05 to 1.

Skinner (*Jour. Chem. Soc.*, lxi., 339) finds ratios varying from 4·00 to 4·37 mean 4·16.

Calculating from the figures in No. 30-34 inclusive, the maximum solubility of fusel oil in fat should be 17·5 per cent., and in the acid mixture 5·9 per cent.

This is an extension of Henry's law of the distribution of a gas between a space and a liquid, and assumes that a substance in solution behaves like a gas; this is in accordance with recent theories of solution (*c.f. Ostwald's Solutions*).

The experiments quoted above furnish *a priori* evidence that after fusel oil, acid, and milk have been mixed as in the conditions of experiment, there is no free alcohol in solution; in connection with this may be noticed the following points :—

- (i.) Fusel oil and butter-fat are miscible in all proportions.
- (ii.) Sulphuric acid combines with alcohols, and fusel oil consists almost wholly of these latter bodies.

As the extension of Henry's law quoted above would not hold good, were free alcohol assumed to exist in solution, the fact that it does hold good by deduction shows that the

fusel oil has disappeared as such. The formation of amyl (propyl, iso-propyl, &c.), hydrogen sulphate is a possible reaction.

Experiments were made to test this assumption, and to confirm, if possible, the figure (5.9 per cent.) calculated for the maximum solubility in the acid mixture. Varying quantities of the fusel mixture were added to 15 c.c. of water, 9 c.c. of acid were poured in, and the mixture shaken; a hot mixture of 2 pts. water and 1 pt. acid was then added till the flask was full (total volume 28 c.c.), with results as follows:—

Volume of fusel mixture.				Result.
35	...	...	3.2 c.c.	Small layer of black particles.
36	...	...	4.7 c.c.	Considerable separation.
37	...	...	3.0 c.c.	Small layer of black particles.
38	...	...	2.5 c.c.	" " " "
39	...	...	3.5 c.c.	Separation of 4 divisions.
40	...	...	3.8 c.c.	Considerable separation.

The limit of solubility is then 3.5 c.c. of the fusel mixture = 1.75 fusel oil; this gives a maximum solubility of 6.1 per cent., which is practically the same as the maximum solubility calculated.

The layers separating in 36 and 40 were examined; they were found to be very nearly soluble in water, about 10 per cent., however, being undissolved, and to give the water an intensely acid reaction; several of the layers of fat obtained in various experiments were also examined by shaking them with water, which always acquired a strong acid reaction, much greater than was given by butter-fat simply treated with strong acid.

These experiments greatly strengthen the view that amyl hydrogen sulphate is formed, which then distributes itself between the acid mixture and the fat in the ratio of the maximum solubility of each.

I have been unable, with the means and time at my disposal, to actually prove that amyl hydrogen sulphate is formed, and to determine its maximum solubility in butter-fat; but the evidence points strongly to the truth of the assumption that I have made, and it explains so satisfactorily the various phenomena observed, that I do not hesitate to adopt it.

The figure for the solubility of fusel oil (as amyl hydrogen sulphate) in the acid mixture would not hold good were the proportions of acid to water varied; and this affords an explanation as to why the results in Series I. differed from those in Series II. The bottles in Series I. were larger than in Series II., and more acid was constantly added in the former than in the latter, and the solubility of the fusel oil thereby increased; added to this, the volume of the acid mixture was also larger, and therefore a less quantity of fusel oil passed into the fat in Series I.

It is important, then, to have the bottles of the same size, or to add a constant amount of each of the re-agents. I have adopted as normal, bottles holding 28 c.c. and proportions, as follows: milk 15 c.c., fusel mixture 3 c.c., sulphuric acid 9 c.c., and for filling up the bottles a hot mixture of 2 pts. water to 1 pt. acid by volume.

In experiments 30 and 33, where 1 c.c. only of fusel mixture was used, it is worthy of note that the fat showed a tendency to solidify on cooling, while in the others it remained liquid till the close of the experiment.

A few experiments, which properly belong to Series III., were made before the importance of adhering strictly to the proportions was realized; as they were partially the means of leading me to search for the laws governing the volumes of fat, I give them:—

No.	Fat		
	Gravimetric.	L. and B.	Corrected.
41.	21.7 C.B.	21.6	20.3
42.	23.2* V.	24.2	22.7
43.	24.0 A.	24.5	23.1
	23.7 W.		
	22.9 V.		
44.	21.4 A.	21.4	20.1
	21.4 S.		
	20.5 V.		

It is seen that the figure read direct from the table is much closer to the actual fat than that corrected by dividing by 1.065, and it was partly to seek an explanation of this that I commenced the experiments recorded above. As the number of creams in series I. and II. was only 7, and it was from the mean of these that the table was calculated by allowing for the decrease of density of the cream as the fat increased, and as the experimental error with creams is multiplied by 5 on account of the dilution, and, further, as only two creams in Series II. were analysed by Adams' method—one of which (No. 21) agreed better with the direct result than the corrected one—the discrepancy between series II. and III., viewed in the light of the discovery of previously unsuspected sources of error, did not seem so serious; it pointed, however, to the necessity of the revision of the table given above by exact experiments.

A comparison of the three series of experiments with Leffmann and Beam's original bottles, shows that Leffmann and Beam in six experiments have, practically, no average error. Hehner finds an average deficiency of 0.06 per cent. in seven experiments, while I (series I neglecting creams) find in fourteen experiments a mean difference of +0.08 per cent. These differences between the results of different operators are probably due to a difference in the average amount, and possibly strength, of acid added, and possibly also to a difference in the fusel oil used.

A series of results was now started, using bottles holding 28 c.c., and adding the re-agents in the proportions given above. Milks only are given in this table.

* Experiments made on mixtures of this cream with skim milk show that it contained about 24 per cent. fat. Vieth's table is not accurate within 1 per cent.

Fat.

No.	Gravimetric.	L. and B.	L. and B. corrected.	Error.
45.	3.48	3.75	3.48	—
46.	2.42	2.6	2.44	+0.02
47.	4.06	4.35	4.09	+0.03
48.	3.09	3.35	3.15	+0.06
49.	3.18	3.43	3.22	+0.04
50.	3.23	3.45 } bottle 29 c.c. 3.45	3.24	+0.01
51.	2.08*	2.45	2.30	+0.22
52.	3.45	3.67	3.45	—
53.	3.54	3.8	3.57	+0.03
54.	3.50	3.75	3.52	+0.02
55.†	4.47	4.95	4.65	+0.18
56.†	5.10	5.3	4.98	—0.12
57.†	2.08	2.32	2.18	+0.10
58.†	3.27	3.67	3.45	+0.18
59.†	3.72	4.1	3.85	+0.13
60.	2.82	3.02	2.84	+0.02
61.	3.56	3.72	3.49	—0.07
62.	.22	.2	.19	—0.03
63.	.20	.25	.23	+0.03
64.	3.64	3.95	3.71	+0.07
65.	4.19	4.3	4.04	—0.15
66.	2.46	2.7	2.53	+0.07
67.	3.25	3.45	3.24	—0.01

The agreement is seen on the whole to be very good. There is, if anything, a tendency to be somewhat high, indicating that the factor used (1.065) is, perhaps, low. The factor 1.07 agrees rather better, but the difference is within the limits of reading. I have pointed out in the foot-notes that there is some explanation to be readily found for the larger discrepancies—*i.e.*, Nos. 51, 55-59 inclusive. The agreement between the fat found by this method and that gravimetrically determined, is as good on the whole as the agreement between duplicate gravimetric determinations obtained in ordinary commercial work, where extreme precautions are not taken to insure exactitude.

There are numerous sources of error, which I enumerate and discuss.

(i.) The milk is measured, not weighed, while the results are calculated as percentages by weight. Vieth (*THE ANALYST*, Vol. xvi., p. 90) has, however, shown that this source of error is very small.

* This was a mixture of skim milk, cream, and water. The fat calculated from the proportions used should be 2.25. This makes me ascribe the large difference to an error in the gravimetric determination.

† These 5 milks were also somewhat sour when analysed, and some difficulty was experienced in properly distributing the cream. This may account for the larger error than usual.

(ii.) The fatty layer is also measured. This makes more difference than the measurement of the milk as the co-efficient of expansion, and possibly the mean variation of the density is larger than in milk. I find, however, that the temperature of the fatty layer, when measured, is about 5° above the laboratory temperature, and a maximum variation of 10° may be expected in this latter. Taking the expansion of this layer to be the same as that of butter, the maximum error would not be more than 0.8 per cent. of the fat—*i.e.*, in ordinary cases the extreme error from this cause would be less than 0.04 per cent. on the milk; actually it would be less, as the measurement of the milk would be influenced by the same cause in the same direction. The maximum variations in the density of butter-fat do not exceed 0.5 per cent. The combined extreme error from these causes would not exceed 0.05 per cent. on the milk.

(iii.) The error of measurement and graduation. As the upper and lower limits are very sharp, the volume of the fatty layer can be read with care and practice to $\frac{1}{4}$ of a division. I find it advisable to take two or three readings as the fatty layer descends owing to the contraction of the hot liquid in the bottle, and take the mean as the correct. It is rare to find a difference in three readings.

(iv.) The variations in the composition of the fatty layer. As already stated, it consists of fat with a certain proportion of (probably) amyl (propyl, &c.) hydrogen sulphate. The exact proportion is governed by the extension of Henry's law given above. The limits of exactitude of this law, or rather the modifying circumstances, I know not. One thing is certain, however; according to this law the proportion of amyl hydrogen sulphate in the fatty layer decreases as the fatty layer increases, as the total quantity of fusel oil added is always the same. The error due to this cause, however, will always be small, as the volume of the fatty layer is very small compared to the total volume, and it may be neglected as it falls within the limits of reading. Lactic acid may be a possible source of error, as it is soluble in fat, and in a very sour milk it may make a small difference. As lactic acid is also soluble in water, and mixtures of acid and water, the error is not likely to be appreciable. It must not be forgotten, also, that the reaction of sulphuric acid on the milk may give rise to compounds soluble in fat.

(v.) The error due to the variations in the proportions used, and in the size of bottles. The variations due to length of time in whirling, and the speed of rotation. These errors may be reduced to a minimum by adhering rigidly to the same proportions. I have not yet had an opportunity of studying the influence of varying any of these, but will do so, and discuss the results in Part II. of this paper.

The total error due to all these causes will not exceed 0.1 per cent. with ordinary care. A method arriving at this exactitude deserves to be considered as more than a rough method; it becomes a reliable one.

The advantages of the method are many: It is extremely rapid, two samples can be comfortably analysed in five minutes, with reliable results. I can recommend it to public

analysts to sort out milk samples which may be sent them. The trouble of making a fat estimation by this method is very little if any more trouble than weighing out the milk, &c., for the determination of total solids. By the determination of the density, also, the solids-not-fat can be estimated by the formula of Hehner and myself (*THE ANALYST*, xiii., 32), or the milk scale (*THE ANALYST*, xiii., 65), with sufficient exactitude to decide whether the milk is, undoubtedly, genuine or suspicious. A great advantage is obtained by this method, as the necessary further determinations can at once be proceeded with while the milk is fresh.

For commercial purposes it is also sufficient; the cost of re-agents is small, and the use of ether, with its objections, is avoided.

For dairy-control purposes it is very useful. It does not, however, fulfil all the requisites of a perfect dairy method; it is essentially a laboratory method. The facts that the reagents used, sulphuric acid and the fusel mixture, are corrosive; the attention to detail necessary—a point not likely to be appreciated by anyone, except he be a chemist; the fragile nature of the essential parts of the apparatus; and, last though far from least, the exothermic reaction—all militate strongly against the use of this apparatus in the dairy. It does not supply the widely-felt need of a universal method; in its proper sphere—the laboratory—I anticipate a future for it.

In Part II. of this paper I propose to consider the analysis of cream by this method, and to study more deeply the laws that govern the process; also, the errors and means of reducing them to a minimum.

In the absence of the author, Dr. Dyer read the following:

SUPPLEMENTARY NOTES ON "A NEW AND RAPID METHOD FOR THE DETERMINATION OF NITROGEN IN ORGANIC BODIES."

By W. F. KEATING STOCK, F.C.S., F.I.C.

In a communication read before the May meeting of the Society of Public Analysts (*see THE ANALYST*, June, 1892, page 109), I pointed out that the nitrogen of certain organic bodies, of which a list was given, could be rapidly converted into ammonia by treatment with manganese dioxide in presence of strong sulphuric acid. I was not present at the meeting, and as the direction of the discussion was distinctly adverse to the method I proposed I feel that it is due to the members who were present on that occasion that I should take the earliest opportunity of showing them that the method is far from being an unimportant one.

A good deal was said about the danger of the ammonia formed being acted upon by the manganese dioxide. Now it will be found on reference to the paper, that in my experiments the relation of manganese dioxide to nitrogen present ranged from 141 to 1 to 66 to 1. Also that the exposure of the substance to the action of the dioxide was not a "time" exposure—that is, the reaction was allowed to proceed until green coloration of the mass ensued without respect to time. And yet the results agreed most perfectly. I

imagined that these considerations were quite sufficient in themselves to dispose of any fear on this point.

It appeared, too, that my not giving details of analyses of pure ammonium salts was considered an important omission, but this was certainly far from what I intended. I meant to show that my method would deal perfectly with *Nitrogen in organic combination*. I said so at the outset, and consistently stuck to my text. But believing that facts are of greater value than argument, I beg to quote the following experiments as further evidence that ammonia is not lost in the "rapid" process:—

Analysis of Ammonium Chloride.

0.4922 grm. taken. Nitrogen calculated, 0.1288 grm. Nitrogen found, 0.1276 grm.

Analysis of Ammonium Oxalate.

0.4934 grm. taken. Nitrogen calculated, 0.0973 grm. Nitrogen found, .0965 grm.

It was stated during the discussion that I had admitted having entirely failed with ferrocyanide. What I said was that "attempts had been made—but so far without success." I knew when I wrote the paper where the want of success lay, and I have since corrected the error, as will, I think, be seen by the following:—

Analysis of Potassium Ferrocyanide.

0.5 grm. taken. Nitrogen calculated, 0.0994 grm. Nitrogen found, 0.0996 grm.

0.5 " " " 0.0994 " " " 0.0996 "

0.5 " " " 0.0994 " " " 0.0988 "

To the statement made that the analyses of uric acid are not in close agreement I hardly think it necessary to reply. A difference of 0.19 per cent. is mild as compared with what one sometimes sees in the data from which the formula of a substance is calculated; and, speaking as an analyst of long experience, I should be glad if I could always get within two-tenths of a per cent. of "the constituent sought."

These, then, were the points in the discussion which seemed to necessitate some further notice at my hands, but I should like to add that analysts have few "universal" processes, and I do not ask the members of this Society to look upon the method of procedure which I have had the honour of laying before them as universally applicable. What I do claim for it is, that with many substances the time needed for oxidation is shortened to 3 or 4 minutes; that it does away with special flasks, ordinary beakers may be used, and this greatly facilitates the work; that it dispenses with the use of mercury and consequently of potassium sulphide; that there is no need for zinc in the distillation and that fracture of the distilling flask is impossible; and, finally, that when thoroughly understood, it is capable of very wide application, yielding results which are perfectly satisfactory. I am myself using the process regularly with a degree of ease, accuracy and speed that I never expected to attain in the determination of nitrogen.

This terminated the Society's proceedings.

The Analysis of Substitutes for Coffee. Moscheles and R. Stelzer. (*Chem. Zeit.* 1892, xvi. 281, 282.)—The property which most readily distinguishes coffee substitutes from genuine coffee is usually their freedom from caffein. Some such substances have been found to contain the bitter principle of the lupin as a substitute for caffein—a most reprehensible addition. Quite recently a coffee surrogate was examined by the authors which contained powdered kola nut, which is known to contain caffein. In distinguishing analytically between coffee and its substitutes the determination of the percentage of fat and of total extractive matter is of value. The amount of fat in coffee varies between 7 and 16 per cent., while in the factitious article it is considerably lower, namely, from 0 to 8%. The total extract from coffee is about 20-30%, while that of coffee substitutes usually varies from 50-75%. The process of analysis is hampered by the difficulty of obtaining a clear solution of the total soluble matter in the coffee, and at the same time making certain of thorough extraction. The filtration of such a solution is difficult, and it commonly becomes turbid on cooling, from the precipitation of gum, dextrin, and similar bodies. The authors have, in consequence, abandoned the attempt to obtain perfect extraction, the more readily because it does not represent what takes place in the actual use of coffee. Their practice is to powder finely 25-30 grms. of the substance and digest it for half-an-hour on the water-bath with 500 c.c. of water. The solution is made up to one litre, allowed to cool and a portion drawn off and evaporated to dryness, with the addition of a weighed quantity of ignited sand, to constant weight. This represents the extract obtained under ordinary domestic conditions. The following results were obtained with some modern coffee surrogates:—

CHICORY MALT COFFEE FROM R. BAER, BERLIN.

Extract	...	...	...	...	...	...	36.00%
Moisture	...	...	...	...	...	...	2.65
Woody fibre	...	...	...	...	...	...	12.93
Natural ash	...	...	...	...	...	...	2.11
Sand	...	...	...	...	...	...	0.05
Soluble proteids	...	...	...	...	...	...	0.25
Gum and dextrin	...	...	...	...	...	...	24.14
Sugar	...	...	...	...	...	...	4.90
Starch, etc.	...	...	...	...	...	...	42.13
Fat	...	...	...	...	...	...	1.84
Caffein	...	...	...	...	...	...	—

	Linde.					Linde Bros. Coffee.	Linde Bros. Coffee Essence.	Feine's Malt Coffee.
Extract	...	...	...	...	...	68.14	72.03	60.33
Soluble proteids	...	...	...	...	...	4.61	4.56	7.56
Sugar and dextrin	...	...	...	...	...	59.38	59.53	59.37
Other extractive substances	...	...	...	...	...	35.81	35.81	33.07
Moisture	...	...	...	...	...	4.63	3.23	2.13
Ash	...	...	...	...	...	5.03	2.35	1.87

COFFEE SUBSTITUTE OF UNKNOWN ORIGIN.

Extract ...	...	...	...	...	...	...	46.52%
Soluble proteids	...	...	...	...	...	...	13.94
Nitrogenous extractive material	...	...	...	...	...	...	5.18
Non-nitrogenous extractive material	...	...	...	...	...	...	18.88
Sugar ...	...	...	...	...	...	...	12.00
Soluble salts	...	...	...	...	...	...	2.32
Moisture	...	...	...	...	...	...	8.01
Fat ...	...	...	...	...	...	...	4.27
Woody fibre	...	...	...	...	...	...	22.04
Natural ash	...	...	...	...	...	...	0.74
Sand ...	...	...	...	...	...	...	0.48
Caffein ...	...	...	...	...	...	...	0.31

In all cases the proteid and extractive substances given above are those in the "extract" which was obtained by the method already described, no attempt at complete extraction being made.

B. B.

The Determination of Crude Fibre. S. Gabiel. (*Zeits. Physiolog. Chem.*, 1892, xvi., 370, through *Chem. Zeit.*)—The author has examined Hönig's method for the determination of crude fibre and starch. The method in question depends upon the fact that albumen and starch become soluble in water, after heating with glycerine to 210° C, while cellulose is not attacked. As the process was employed by the author solely for the determination of crude fibre, the whole of the operations for the separation of the starch could be omitted. In place of the sulphuric acid bath, used by Hönig, the author found that a naked flame could be more conveniently employed, as regulation of the temperature was thereby rendered easier. Certain modifications were necessary, on account of the nitrogenous and non-nitrogenous substances, other than cellulose, being unattacked by glycerine alone. The requisite additional activity of the attacking reagent can be obtained by the use of a caustic alkali, and the method thus modified, is carried out as follows:—2 grms. of the substance are heated, in a 250 c.c. flask, on a piece of wire netting, over a naked flame, with 60 c.c. of a solution of caustic alkali in glycerine, containing 33 grms. of caustic potash per litre. A vigorous reaction sets in usually at about 130° C, at which point precaution is necessary to moderate the foaming that takes place. At a temperature of 160° C, the reaction is for the most part finished, after which the temperature is gradually raised to 180° C. The product is then emptied into a dish containing 200 c.c. of boiling water, well stirred, allowed to settle thoroughly, and the supernatant liquor drawn off with a syphon, having a piece of linen tied over the end. The residue is then boiled up again with 200 c.c. of water, and a third time with the same quantity of water, to which has been added 5 c.c. of 25 per cent., hydrochloric acid. The unattacked crude fibre is washed with alcohol and ether, as in the Wendeer method. The extremely small quantity of nitrogenous substances left in the crude fibre appears to be, in most cases, negligible.

B. B.

A Simple Method for the Detection of Frozen Meat. Maljean. (*J. Pharm. Chim.*, 1892, xxv. 348, through *Chem. Zeit.*)—The process adopted by the author for distinguishing between fresh meat and that which has been preserved in the frozen state, consists in expressing a little blood or meat juice from the sample, and examining it under the microscope. The whole operation must be performed quickly, in order to prevent any drying up of the liquid under examination. When the juice of fresh flesh is thus examined, it is seen to contain numerous red corpuscles, which are normal in colour, and float in a clear serum. In the case of blood from frozen flesh, the corpuscles have dissolved in the serum under the influence of the low temperature, and not a single normal red corpuscle can be seen. The hæmoglobin escapes into the serum, and appears as irregular, yellow-brown crystals. These may be frequently seen by the naked eye, but, in every case, can be readily detected under the microscope. B. B.

The Determination of Glycerine in Wine. M. T. Lecco. (*Chem. Zeit.*, 1892, xvi., 504.)—The usual method of determining glycerine in wine is that officially recognised by the Berlin Committee of 1884, although it is far from ideal. The residue which is obtained by evaporating the wine together with quartz sand and milk of lime nearly to dryness, is difficult to remove from the dish in which the evaporation has been performed, and a certain quantity of glycerine is apt to be left in the residue after extraction. The following are the modifications proposed by the author:—10 c.c. of the wine are well mixed with 0.1 of a grm. of powdered calcium hydrate, 10 grms. of quartz sand added, and the whole evaporated almost to dryness on the water bath. The residue is extracted four or five times with hot absolute alcohol, and the extract, amounting to 40—50 c.c., is filtered into a flask holding about 100 c.c., then evaporated on the water bath the syrupy residue dissolved in 5 c.c. of alcohol, 7.5 c.c. of ether added, the flask well corked, allowed to stand some hours, and the clear solution poured into a weighed flask (previously filtering if necessary), the alcoholic liquid evaporated off, and the residue dried for one hour in the water oven and weighed. This method, when tried on seven samples of Servian wine, containing from 0.7 to 1.0 per cent. of glycerine, gave results ranging from 0.1 to 0.36 per cent. higher than the old method; while, at the same time, closely concordant results were obtained by repetitions of the new method, and also when it was carried out on a scale ten times as great as that prescribed above. In order to ascertain whether the compound formed of lime and glycerine by evaporation to complete dryness resisted the solvent action of the alcohol, further experiments were made in which this condition obtained, with the result that the percentage of glycerine found was not diminished, but slightly increased. Should this observation be confirmed, the need for special precaution in the evaporation will be obviated. The author also states that he has obtained good results by evaporating an aliquot portion of the alcoholic extract, by which means previous filtration and washing necessary to the original process are avoided. He has yet to prove the purity of the glycerine thus isolated. B. B.

LEGAL.

SALE OF COFFEE AND CHICORY.

JONES *v.* THE VESTRY OF BERMONDSEY.

An appeal case, arising out of the judgment delivered by Mr. Slade in a case of the sale of a mixture of coffee and chicory, was heard before Sir Peter Edlin, Q.C., on June the 15th, 1892. The case as stated by Mr. Slade was as follows :—

“In this case the prosecutor entered the shop of the defendant, a grocer, and asked for a quarter of a pound of coffee. The assistant inquired, ‘A quarter of a pound of shilling?’ He said, ‘Yes,’ and was served with a mixture in a brown paper parcel, for which he paid 3d. On analysis the mixture was found to contain 40 per cent. of coffee and 60 per cent. of chicory. On the outside of the wrapper were legibly printed these words: ‘This is sold as a mixture of chicory and coffee.’ This was admitted to be a sufficient protection to the vendor under the Food and Drugs Act, unless it could be shown there was a fraudulent intent under the 8th section of the Act. It was proved before me that the cost of pure coffee is 1s. 4d. per lb., and of chicory 4d. per lb., so that the mixture cost the vendor about 9½d. per lb., which he retailed to the customer at 1s. per lb. So it comes to this—first, the article asked for is not supplied; second, the shop-keeper cannot be punished since he protects himself by a label, unless fraud is proved; and third, the customer is not prejudiced financially because he gets his money’s worth. It appears that coffee is generally mixed with chicory, and that pure coffee (like pure mustard) is hardly known as an article of domestic use; and it is legal to sell a mixture if proper precaution is taken. But here the 8th section of the Act steps in, which says that nothing shall be added which is intended fraudulently to increase its bulk, weight, or measure, or conceal its inferior quality.’ And why? Because a customer is entitled to get the article which he asked for. The mere use of the label opens the door to fraud. It is very difficult to draw the line as to the proportion of the ingredient. I am aware of the cases of *Lydiard v. Reece*, *Horder v. Meddings*, and *Horder v. Adams*. These cases seem to show that fraud is purely a question of fact for the magistrates to decide. After much deliberation I have come to the conclusion that the presence of a larger proportion of the inferior ingredient as disclosed in this case (though not excessive) is sufficient to bring it within the mischief aimed at by the 8th section of the Act, and that to hold otherwise would render nugatory the provision which was passed for the protection of the poorer classes. The defendant will be fined £3, and will have to pay 12s. 6d. costs.”

After the case had been argued at considerable length (two days) before Sir Peter Edlin, the following judgment was delivered :—

“ I have arrived at the conclusion that this conviction should be upheld. I would in the first place refer to what has been recorded as inaccuracy in the conviction, which describes this as an article of drink. It may be more properly described as an article of food. It would not become drink until water is mixed with it. Therefore the word ‘drink’ which occurs twice in this conviction must be altered to ‘food.’ Let it be understood that this correction is made. Now with regard to the judgment of the learned magistrate, Mr. Wyndham Slade. In substance I agree with it; I agree with him in the conclusion at which he arrives after an obviously very careful consideration of the facts as they were laid before him. We here have had the advantage of hearing other witnesses, and, if I am not mistaken, more witnesses than were called before Mr. Slade; but I do not think that what they have stated could have materially altered the facts as they were disclosed before the learned magistrate. I must say I am unable to follow him, for judging from what appears in this copy of his judgment he says that this sale was not prejudicial financially to Mr. Toogood. It seems to me that, from the very nature of the mixture that was sold to him, he would be prejudiced, as it would seem from what he has himself admitted that when he accepted the mixture, having asked for coffee, he was not aware of the proportion of the two ingredients—chicory and coffee. He did not know there was an undue proportion, namely, 60 per cent. of chicory and only 40 per cent. of coffee. We have it proved before us, and it cannot be denied, that even if this mixture had been equal in the proportions, that is to say, the same amount of coffee as there was of chicory, the profit to Mr. Jones would be 2d. in the 1s. And we have it proved, moreover, that for coffee when sold, the cheapest coffee that is retailed, the profit is only 2d. in 1s. 6d., and that chicory when sold realised a profit of 2d. in respect of 6d. So that it is obvious when we have regard to the disproportion shown here—the much larger proportion of chicory to coffee in the mixture actually sold—that it is distinctly to the prejudice of the buyer that he should purchase that mixture instead of having an equal weight of two several ingredients, of which the article is composed. Then we have to consider what were those proportions—what we may fairly consider were those proportions, and what probable profit they would bring to the seller; and we find that upon a shillingsworth it would bring to him a profit of 3d. and some four-fifths of a farthing. Without going into the fractions we may say there was a clear profit of 25 per cent., whereas if the two articles were sold separately the profit would be only 4d. in 2s., or one-sixth. Now, having regard to the great disproportion in the value of the several ingredients, it seems to me to be the duty of the seller to take care—if I may say so, extra care—if he sells, as he lawfully may do, a mixture of chicory and coffee, to disclose to his buyer that it is a mixture. It is incumbent upon him also to take care that the mixture is in due proportions, and that there is not that excess of the cheaper article which, having regard to the price, would operate prejudicially to the purchaser of the coffee. Then we have to ask ourselves upon

the facts before us whether the appellant has brought himself in this transaction within the saving provision of the 8th section of the Act. I should be loth to say I could come to a conclusion that there had been an intention of fraud, but I do think that sufficient has been shown in this case to disentitle him to say that there was not that fraudulent admixture—that the mixture was not of such inferior quality as entitles him to the benefit of this saving clause of the 8th section of the Act of Parliament. I think, therefore, that Mr. Slade was right in his conclusion that this was a sale to the prejudice of the buyer. Now Mr. Slade's expressions are deserving of notice. They indicate the care which he had bestowed upon the case, and I may endorse it as a substantially correct view of what I take in this case. He said: 'After much deliberation I have come to the conclusion that the presence of the larger proportion of the inferior ingredient as disclosed in this case (though not excessive) is sufficient to bring it within the scope of the 8th section.' I concur in that expression, and I agree also with him in holding that 'otherwise it would render nugatory the provision which was passed for the protection of the poorer classes.' This provision was passed for the protection of the buyer, and if the seller is desirous of availing himself of the provision in the 8th section, he must be careful to do so in such a way as gives full notice to the purchaser of what he is buying; and he must be careful also that he is not so compounding the ingredients as to constitute it an article of inferior quality to that which he is professing to sell. I cannot think that the expression of the words of the label, 'A mixture of chicory and coffee,' would indicate to any purchaser that the mixture was in an undue proportion of 60 per cent. of the cheaper article—the much cheaper article—and only 40 per cent. of coffee as in this case. For these reasons I think the magistrate came to a right conclusion, and I must confirm this conviction."

Defendant's counsel asked his lordship to state a case for the Court of Queen's Bench. Sir Peter at first declined, as he was doubtful whether the High Court would entertain the case; but upon being pressed, he promised to further consider the matter with a view to presenting the case in such a manner to the judges, that there would be some probability of their entertaining it.

SAMPLES OF MILK TAKEN FOR ANALYSIS.

ROLPH *v.* THOMPSON.

On February the 27th, 1892, an inspector under the Food and Drugs Act intercepted six churns of milk consigned to a London milk dealer, which had arrived at King's Cross station from the country. He took a sample from each churn, and divided it into two parts; one portion he forwarded to the Public Analyst, the other he retained himself. Prosecutions for adulteration were instituted in each case, and dismissed by the magistrate on the ground that the samples should have been delivered whole to the analyst, the division of the samples constituting an irregularity. An appeal was carried to the Court of Queen's Bench, and heard on June 16th, when Mr. Justice Grantham and Mr. Justice Charles expressed the opinion that the magistrate's decision was wrong and that the fact

of the inspector dividing the samples did not affect the proper delivery to the analyst. The case was therefore remitted back to the magistrate.

REVIEW.

FARM-YARD MANURE: Its Nature, Composition and Treatment. By C. M. AIKMAN, M.A., B.Sc., F.R.S.E. (Wm. Blackwood and Sons, Edinburgh and London.) 1s. 6d.

THIS is really a section, published in advance, of a large work on "Soils and Manures," on which the author is still engaged. The little volume now under notice gives evidence of thorough literary labour, and augurs well for the value of the complete work, of which it forms the first instalment. While freely acknowledging his indebtedness to the authors of existing manuals of agriculture and agricultural chemistry, Mr. Aikman has evidently spent pains, by the study of contemporary work, in bringing his monograph up to date. In these days of cheap artificial manures and cheap food, farmyard manure is, perhaps, a less vital subject of interest to the farmer than it used to be. "Muck" will always have its special functions—those affecting the very important physical features of the soil—which can, perhaps, be performed by no other agent. But its quality, in the sense of its actual chemical fertilising strength, is of less importance than in the days that preceded cheap nitrate of soda and abundant artificial phosphates. We do not suggest that sensible farmers would take less pains now than formerly, to preserve the full value of the manure-heap, but that probably fewer advanced farmers find it worth while to take the thought that they would once have taken in order to enrich it. With nitrate of soda at 8s. 6d. per cwt., it would scarcely pay to use a more expensive nitrogenous food to fatten stock in place of a cheaper farinaceous one, *merely* for the sake of strengthening the "dung." Nevertheless, if the chemistry of farm-yard manure has not at the moment the full economical importance that it once had, it is, at the same time, desirable that every farmer should have some knowledge of its principles, and indispensable that the real student of the science of agriculture should have a clear insight into them. This little book will be found interesting, either to the light or to the careful reader, and, to study the convenience of both, Mr. Aikman has separated most of his tabular and statistical matter from the general context, and placed it in an appendix. The small price at which the book is published should lead to its taking a place, in advance of the larger work that we are promised, on the shelf devoted to agricultural text-books in every library where such a shelf exists.

APPOINTMENT.

Mr. Arthur E. Ekins, F.C.S., of St. Albans, has been appointed by the Herts County Council public analyst for Hertfordshire, exclusive of the city of St. Albans.